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Decolorisation of Textile Dyeing Effluents Using Advanced Oxidation Processes

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1. Introduction

Textile industry is a leading industry for most countries, such as China, Singapore, UK, Bangladesh, Italy, Turkey etc. But, environmental pollution is one of the main results of this industry. Parallel to usage of huge amounts of water and chemicals, the textile dyeing and finishing industry is one of the major polluters among industrial sectors, in the scope of volume and the chemical composition of the discharged effluent (Pagga & Brown, 1986).

Textile industry effluents can be classified as dangerous for receiving waters, which commonly contains high concentrations of recalcitrant organic and inorganic chemicals and are characterised by high chemical oxygen demand (COD) and total organic carbon (TOC), high amounts of surfactants, dissolved solids, fluctuating temperature and pH, possibly heavy metals (e.g. Cu, Cr, Ni) and strong colour (Grau, 1991, Akal Solmaz et al., 2006).

The presence of organic contaminants such as dyes, surfactants, pesticides, etc. in the hydrosphere is of particular concern for the freshwater, coastal, and marine environments because of their nonbiodegradability and potential carcinogenic nature of the majority of these compounds (Demirbas et al., 2002, Fang et al., 2004, Bulut & Aydin, 2006, Mahmoudi & Arami, 2006, Mahmoudi & Arami, 2008, Mozia et al., 2008, Li et al., 2008, Atchariyawut et al., 2009, Mahmoudi & Arami, 2009a, Mahmoudi & Arami, 2009b, Mahmoudi & Arami, 2010, Amini et al., 2011). The major concern with colour is its aesthetic character at the point of discharge with respect to the visibility of the receiving waters (Slokar & Le Marechal, 1997).

The main reason of colour in textile industry effluent is the usage of large amounts of dyestuffs during the dyeing stages of the textile-manufacturing process (O'neil et al., 1999, Georgiou et al., 2002). Inefficient dyeing processes often result in significant dye residuals being presented in the final dyehouse effluent in hydrolysed or unfixed forms (Yonar et al., 2005). Apart from the aesthetic problems relating to coloured effluent, dyes also strongly absorb sunlight, thus impeding the photosynthetic activity of aquatic plants and seriously threatening the whole ecosystem. Stricter regulatory requirements along with an increased public demand for colour-free effluent necessitate the inclusion of a decolorisation step in wastewater treatment plants (Kuo, 1992).

Well known and widely applied treatment method for the treatment of textile industry wastewater is activated sludge process and its modifications. Combinations of activated sludge process with physical and chemical processes can be found in most applications. These traditional treatment methods require too many spaces and are affected by

wastewater flow and characteristic variations. But, either activated sludge process modifications itself or combinations of this process with physical or chemical processes are inefficient for the treatment of coloured waste streams (Venceslau et al., 1994, Willmott et al., 1998, Vendevivere et al., 1998, Uygur & Kok, 1999).

On the other hand, existing physico-chemical advanced treatment technologies such as, membrane processes, ion exchange, activated carbon adsorption etc. can only transfer pollutants from one phase the other phase rather than eliminating the pollutants from effluent body. Recovery and reuse of certain and valuable chemical compounds present in the effluent is currently under investigation of most scientists (Erswell et al., 2002). At this point, The AOPs show specific advantages over conventional treatment alternatives because they can eliminate non-biodegradable organic components and avoid the need to dispose of residual sludge. Advanced Oxidation Processes (AOPs) based on the generation of very reactive and oxidizing free radicals, especially hydroxyl radicals, have been used with an increasing interest due to their high oxidant power (Kestioglu et al., 2005). In this chapter, discussion and examples of colour removal from textile effluent will be focused on those of most used AOPs.

2. Advanced Oxidation Processes: Principles and definitions

Advanced Oxidation Processes (AOPs) are defined as the processes which involve generation and use of powerful but relatively non-selective hydroxyl radicals in sufficient quantities to be able to oxidize majority of the complex chemicals present in the effluent water (Gogate & Pandit, 2004a, EPA, 1998). Hydroxyl radicals ($\text{OH}\cdot$) has the highest oxidation potential (Oxidation potential, E_0 : 2.8 eV vs normal hydrogen electrode (NHE)) after fluorine radical. Fluorine, the strongest oxidant (Oxidation potential, E_0 : 3.06 V) cannot be used for wastewater treatment because of its high toxicity. From these reasons, generation of hydroxyl radical including AOPs have gained the attention of most scientists and technology developers.

The main and short mechanism of AOPs can be defined in two steps: (a) the generation of hydroxyl radicals, (b) oxidative reaction of these radicals with molecules (Azbar et al., 2005). AOPs can convert the dissolved organic pollutants to CO_2 and H_2O . The generation of highly effective hydroxyl radical might possibly be by the use of UV, UV/ O_3 , UV/ H_2O_2 , $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, $\text{TiO}_2/\text{H}_2\text{O}_2$ and a number of other processes (Mandal et al., 2004).

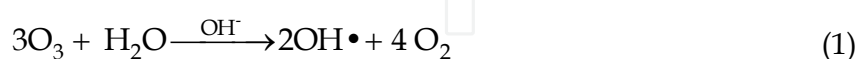
AOPs can be classified in two groups: (1) Non-photochemical AOPs, (2) Photochemical AOPs. Non-photochemical AOPs include cavitation, Fenton and Fenton-like processes, ozonation at high pH, ozone/hydrogen peroxide, wet air oxidation etc. Short description of some important AOPs are given below. Photochemical oxidation processes include homogeneous (vacuum UV photolysis, UV/hydrogen peroxide, UV/ozone, UV/ozone/hydrogen peroxide, photo-Fenton etc), and heterogeneous (photocatalysis etc) processes.

2.1 Non-photochemical oxidation processes

Non-photochemical oxidation processes can be classified as (1) Ozonation, (2) Ozone/Hydrogen Peroxide, (3) Fenton Process, (4) Electrochemical Oxidation, (5) Supercritical water oxidation, (6) Cavitation, (7) Electrical discharge-based nonthermal plasma, (8) gamma-ray, (9) x-ray and (10) electron beam. Ozonation, ozone/hydrogen peroxide and Fenton-process are widely applied and examined processes for the treatment of textile effluent. From this reason, brief explanations and examples are given below.

2.1.1 Ozonation

Ozone is well known and widely applied strong oxidizing agent for the treatment of both water and wastewater, in literature and on site. Ozone has high efficiency at high pH levels. At these high pH values (>11.0), ozone reacts almost indiscriminately with all organic and inorganic compounds present in the reacting medium (Steahelin & Hoigne, 1982). Ozone reacts with wastewater compounds in two different ways namely direct molecular and indirect radical type chain reactions. Both reactions occur simultaneously and hence reaction kinetics strongly depend on the characteristics of the treated wastewater (e.g. pH, concentrations of initiators, promoters and scavengers (Arslan & Balcioglu, 2000). Simplified reaction mechanisms of ozone at high pH is given in below;



2.1.2 Ozone/hydrogen peroxide (peroxone) process ($\text{O}_3/\text{H}_2\text{O}_2$)

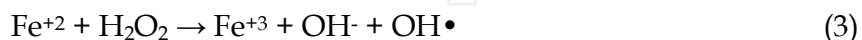
The combination of ozone and hydrogen peroxide is used essentially for the contaminants which oxidation is difficult and consumes large amounts of oxidant. Because of the high cost of ozone generation, this combination make the process economically feasible (Mokrini et al., 1997). The capability of ozone to oxidise various pollutants by direct attack on the different bonds (C=C bond (Stowell & Jensen, 1991), aromatic rings (Andreozzi et al., 1991) is further enhanced in the presence of H_2O_2 due to the generation of highly reactive hydroxyl radicals ($\cdot\text{OH}$). The dissociation of H_2O_2 results in the formation of hydroperoxide ion, which attacks the ozone molecule resulting in the formation of hydroxyl radicals (Forni et al., 1982, Steahelin & Hoigne, 1985, Arslan & Balcioglu, 2000). General mechanism of peroxon process is given below:



The pH of solution is also critical for the process efficiency like other AOPs. Addition of hydrogen peroxide to the aqueous O_3 solution at high pH conditions will result in higher production rates of hydroxyl radicals (Glaze & Kang, 1989). Independence of peroxone process from any light source or UV radiation gives a specific advantage to this process that it can be used in turbid or dark waters.

2.1.3 Fenton process

The dark reaction of ferrous iron (Fe(II)) with H_2O_2 known as Fenton's reaction (Fenton 1894), which is shown in Eq.-15, has been known for over a century (EPA, 2001).



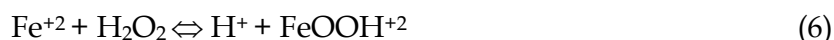
The hydroxyl radical thus formed can react with Fe(II) to produce ferric ion (Fe(III)) as shown in Eq.-16;



Alternatively, hydroxyl radicals can react with and initiate oxidation of organic pollutants in a waste stream,



At value of pH (2.7–2.8), reactions can result into the reduction of Fe^{+3} to Fe^{+2} (Fenton-like).



proceeding at an appreciable rate. In these conditions, iron can be considered as a real catalyst (Andreozzi et al., 1991).

At pH values <4.0, ferrous ions decompose H_2O_2 catalytically yielding hydroxyl radicals most directly. However, at pH values higher than 4.0, ferrous ions easily form ferric ions, which have a tendency to produce ferric hydroxo complexes. H_2O_2 is quite unstable and easily decomposes itself at alkaline pH (Kuo, 1992).

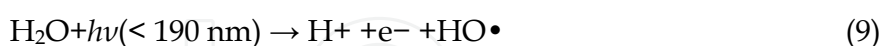
Fenton process is cost-effective, easy to apply and effective for the degradation of a wide range of organic compounds. One of the advantages of Fenton's reagent is that no energy input is necessary to activate hydrogen peroxide. Therefore, this method offers a cost-effective source of hydroxyl radicals, using easy-to-handle reagents (Bautista et al., 2007). The Fenton process consists of four stages. At first, pH is adjusted to low pH. Then the main oxidation reactions take place at pH values of 3–5. The wastewater is then neutralized at pH of 7–8, and, finally, precipitation occurs (Bigda, 1995, Lee & Shoda, 2008). Furthermore, it commonly requires a relatively short reaction time compared with other AOPs. Thus, Fenton's reagent is frequently used when a high reduction of COD is required (Bigda, 1995, Bautista et al., 2007, Lee & Shoda, 2008, Yonar, 2010).

2.2 Photochemical oxidation processes

2.2.1 Homogeneous photochemical oxidation processes

2.2.1.1 Vacuum UV (VUV) photolysis

The Vacuum Ultraviolet range is absorbed by almost all substances (including water and air). Thus it can only be transmitted in a vacuum. The absorption of a VUV photon causes one or more bond breaks. For example, water is dissociated according to;



Photochemistry in the vacuum-ultraviolet (VUV) spectral domain (approx. 140–200 nm) is of high applicatory interest, e.g. (i) in microelectronics, where materials with surface structures of high spatial resolution provide a basis for the fast development of high computational and electronic and optical storage capacities or (ii) in environmental techniques, in particular for the production of ultra pure water and for the oxidative treatment of waste gas and water (Bolton, 2002, Gonzaleza et al., 2004). VUV-photolysis can be achieved by the usage of either a monochromatic (Xe-eximer Xe_2^*) or polychromatic (Hg) radiation sources. These light sources have some limitations such as high price, wave length variations etc. From these reasons application of VUV photolysis are too limited.

2.2.1.2 Hydrogen peroxide/UV ($\text{H}_2\text{O}_2/\text{UV}$) process

This method is based on the direct photolysis of hydrogen peroxide molecule by a radiation with a wavelength between 200–300 nm region. The main reaction of $\text{H}_2\text{O}_2/\text{UV}$ is given below:



The low, medium and high pressure mercury vapor lamps can be used for this process because it has significant emittance within 220-260 nm, which is the primary absorption band for hydrogen peroxide. Most of UV light can also be absorbed by water. Low pressure mercury vapour lamps usage can lead to usage of high concentrations of H_2O_2 for the generation of sufficient hydroxyl radical. However, high concentrations of H_2O_2 may scavenge the hydroxyl radical, making the H_2O_2 /UV process less effective. Some more variables such as temperature, pH, concentration of H_2O_2 , and presence of scavengers affect the production of hydroxyl radicals (EPA, 1998, Bolton, 2001, Mandal et al., 2004 Azbar et al., 2005).

2.2.1.3 Ozone/UV (O_3 /UV) process

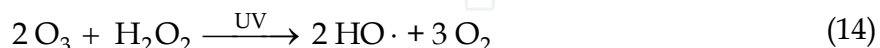
Photolysis of ozone in water with UV radiation in the range of 200-280 nm can lead to yield of hydrogen peroxide. Hydroxyl radicals can be generated by these produced hydrogen peroxide under UV radiation and/or ozone as given equations below:



Starting from low pressure mercury vapour lamps all kind of UV light sources can be used for this process. Because, O_3 /UV process does not have same limitations of H_2O_2 /UV process. Low pressure mercury vapor UV lamps are the most common sources of UV irradiation used for this process. Many variables such as pH, temperature, scavengers in the influent, turbidity, UV intensity, lamp spectral characteristics and pollutant type(s) affect the efficiency of the system (EPA, 1998, Azbar, 2005). Number of laboratory, pilot and full scale applications of Ozone/UV and Hydrogen peroxide/UV processes can be found in literature. Commercial applications of these processes can also be available.

2.2.1.4 Ozone/hydrogen peroxide/UV ($\text{O}_3/\text{H}_2\text{O}_2$ /UV) process

This method is considered to be the most effective and powerful method which provides a fast and complete mineralisation of pollutants (Azbar, 2005, Mokrini et al., 1997). Similar to other ozone including AOPs, increasing of pH affects the hydroxyl radical formation. Additional usage of UV radiation also affects the hydroxyl radical formation. Efficiency of ozone/hydrogen peroxide/UV process is being much more higher with addition of hydrogen peroxide (Horsch, 2000, Contreras et al., 2001). Main short mechanism of $\text{O}_3/\text{H}_2\text{O}_2$ /UV process is given below:



2.2.1.5 Photo-Fenton process

The combination of Fenton process with UV light, the so-called photo-Fenton reaction, had been shown to enhance the efficiency of Fenton process. Some researchers also attributed this to the decomposition of the photo active $\text{Fe}(\text{OH})^{+2}$ which lead to the addition of the $\text{HO}\cdot$ radicals (Sun & Pignatello, 1993, He & Lei, 2004). The short mechanism of photo-Fenton reaction is given below:



With $\text{Fe}(\text{OH})^{2+}$ being the dominant $\text{Fe}(\text{III})$ species in solution at pH 2-3. High valence Fe intermediates formed through the absorption of visible light by the complex between $\text{Fe}(\text{II})$ and H_2O_2 are believed to enhance the reaction rate of oxidation production (Pignatello, 1992, Bossmann et al., 2001).

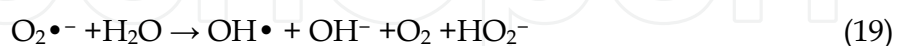
2.2.2 Heterogeneous Photochemical Oxidation processes

Widely investigated and applied Heterogeneous Photochemical Oxidation processes are semiconductor-sensitized photochemical oxidation processes.

Semiconductors are characterized by two separate energy bands: a low energy valence band (h^+_{VB}) and a high-energy conduction (e^-_{CB}) band. Each band consists of a spectrum of energy levels in which electrons can reside. The separation between energy levels within each energy band is small, and they essentially form a continuous spectrum. The energy separation between the valence and conduction bands is called the band gap and consists of energy levels in which electrons cannot reside. Light, a source of energy, can be used to excite an electron from the valence band into the conduction band. When an electron in the valence band absorbs a photon, the absorption of the photon increases the energy of the electron and enables the electron to move into one of the unoccupied energy levels of the conduction band (EPA, 1998).

Semiconductors that have been used in environmental applications include TiO_2 , strontium titanium trioxide, and zinc oxide (ZnO). TiO_2 is generally preferred for use in commercial APO applications because of its high level of photoconductivity, ready availability, low toxicity, and low cost. TiO_2 has three crystalline forms: rutile, anatase, and brookite. Studies indicate that the anatase form provides the highest hydroxyl radical formation rates (Korrmann et al., 1991, EPA, 1998).

The photo-catalyst titanium dioxide (TiO_2) is a wide band gap semiconductor (3.2 eV) and is successfully used as a photo-catalyst for the treatment of organic pollutants (Hsiao et al., 1983, Korrmann et al., 1991, Zahhara, 1999). Briefly, for TiO_2 , the photon energy required to overcome the band gap energy and excite an electron from the valence band to the conduction band can be provided by light of a wavelength shorter than 387.5 nm. Simplified reaction mechanisms of TiO_2/UV process is given in following equations (eq. 16- eq. 19).



The overall result of this reversal is generation of photons or heat instead of $-\text{OH}$. The reversal process significantly decreases the photo-catalytic activity of a semiconductor (EPA, 1998). Main advantage of TiO_2/UV process is low energy consumption which sunlight can be used as a light source.

3. Characterisation of textile industry wastewater

Textile industry produces large amounts of liquid by-products. Volume and composition of these wastewater can vary from one source to other source. In the scope of volume and the chemical composition of the discharged effluent, the textile dyeing and finishing industry is

one of the major polluters among industrial sectors. Textile industry dyes are intentionally designed to remain photolytically, chemically and biochemically stable, and thus are usually not amenable to biodegradation (Pagga & Braun, 1986). Like many other industrial effluents, textile industry wastewater varies significantly in quantity, but additionally in composition (Correira et al., 1994).

These wastes include both organic and inorganic chemicals, such as finishing agents, carriers, surfactants, sequestering agents, leveling agents etc. From these reasons, textile effluents are characterized with high COD ($\approx 400\text{--}3.000\text{ mg/L}$), BOD₅ ($\approx 200\text{--}2.000\text{ mg/L}$), Total Solids ($\approx 1.000\text{--}10.000\text{ mg/L}$), Suspended Solids ($\approx 100\text{--}1.000\text{ mg/L}$), TKN ($\approx 10\text{--}100\text{ mg/L}$), Total Phosphorus ($\approx 5\text{--}70\text{ mg/L}$), Conductivity ($1.000\text{--}15.000\text{ mS/cm}$) and pH ($\approx 5\text{--}10$ usually basic) (Grau, 1991, Pagga ad Braun, 1991, Kuo, 1992, Correira et al., 1994, Arslan and Balcioglu, 2000, , Nigam et al., 2000, Azbar et al., 2005, Akal Solmaz et al., 2006, Yonar et al., 2006, Mahmoudi & Arami, 2009, Yonar, 2010,).

Another important problem of textile industry wastewater is color. Without proper treatment of coloured wate, these dyes may remain in the environment for a long time (Yonar et al, 2005). The problem of colored effluent has been a major challenge and an integral part of textile effluent treatment as a result of stricter environmental regulations. The presence of dyes in receiving media is easily detectable even when released in small concentrations (Little et al., 1974, Azbar et al., 2004). This is not only unsightly but dyes in the effluent may have a serious inhibitory effect on aquatic ecosystems as mentioned above (Nigam et al., 2000).

Definition and determination of colour is another important point for most water and wastewater samples. Some methods can be found in literature for the determination of colour in samples. But, selection of true method for the determination of colour is very important. According to "Standard Methods for the Examination of Water and Wastewater" (APHA- AWWA, 2000), importance of colour is defined with some sentences given below:

"Colour in water may result from the presence of natural metallic ions (iron and manganese), humus and peat materials, plankton, weeds, and *industrial wastes*. Colour is removed to make a water suitable for general and industrial applications. Coloured industrial wastewaters may require colour removal before discharge into watercourses."

From these reasons, colour content should be determined carefully. In Standard Methods, colour content of water and wastewater samples can be determined with four different methods such as (i) Visual Comparison Method, (ii) Spectrometric Method, (iii) Tristimulus Filter Method, and (iv) ADMI Tristimulus Filter Method. Selection of true and appropriate method for samples is very important. Visual comparison method is suitable for nearly all samples of potable water. This method is also known as Platinum/Cobalt method. Pollution by ceratin industrial wastes may produce unusual colour that can not be easily matched. In this case, usage of instrumental methos are appropriate for most cases. A modification of the spectrometric and tristimulus methods allows calculation of a single colour value representing uniform cromaticity differences even when the sample exhibits colour significantly different from that of platinum cobalt standards (APHA-AWWA, 2000).

4. Colour removal from textile industry wastewater by AOPs

Most commonly applied treatment flow scheme for textile effluent in Turkey and other countries generally include either a single activated sludge type aerobic biological

treatment or combination of chemical coagulation and flocculation + activated sludge process (Yonar et al., 2006). Furthermore, it is well known that aerobic biological treatment option is ineffective removal for colour removal from textile wastewater in most cases and the chemical coagulation and flocculation is also not effective for the removal of soluble reactive dyestuffs. Therefore, dyes and chemicals using in textile industry in effluent may have a serious inhibitory effect on aquatic ecosystems and visual pollution on receiving waters, as mentioned above (Venceslau et al., 1994, Willmott et al., 1998, Vendevivere et al., 1998).

There are several alternative methods used to decolorize the textile wastewater such as various combinations of physical, chemical and biological treatment and colour removal methods, but they cannot be effectively applied for all dyes and these integrated treatment methods are not cost effective. Advanced Oxidation Processes (AOPs) for the degradation of non-biodegradable organic contaminants in industrial effluents are attractive alternatives to conventional treatment methods and are capable of reducing recalcitrant wastewater loads from textile dyeing and finishing effluents (Galindo et al., 2001, Robinson et al., 2001, Azbar et al., 2004, Neamtu et al., 2004). In this section, applied AOPs for colour removal from textile effluent are given. Technological advantages and limitations of these AOPs is also discussed.

4.1 Colour removal with non-photochemical AOPs

Ozonation at high pH, ozone/hydrogen peroxide and Fenton processes are widely applied and investigated AOPs for colour removal from textile effluents and textile dyes. As it can be clearly seen from former sections, ozone can produce hydroxyl radicals at high pH levels. According to this situation, pH is very important parameter for ozonation process. As it was described above, under conditions aiming hydroxyl free radical ($\text{HO}\bullet$) production (e.g., high pH), the more powerful hydroxyl oxidation starts to dominate (Hoigne & Bader, 1983). Since the oxidation potential of ozone reportedly decreases from 2.07mV (acidic pH) to 1.4mV (basic pH) (Muthukumanar et al., 2001), it is clear that another more powerful oxidant ($\text{HO}\bullet$) is responsible for the increase in the dye degradation, with a consequent colour absorbance decrease. The efficiency of ozonation in the removal of colour and COD from textile wastewater is important to achieve to discharge limits (Somensia et al., 2010).

Textile wastewaters is very complex due to the organic chemicals such as many different dyes, carriers, biocides, bleaching agents, complexion agents, ionic and non-ionic surfactants, sizing agents, etc. As a result, it is hard to explain the overall degradation of the organic matter by ozone in textile wastewater individually. Thus, some global textile wastewater parameters such as color, COD and dissolved organic carbon are used for the degradation kinetic of organic matter by ozonation (Sevimli & Sarikaya, 2002, Selcuk, 2005).

Textile wastewaters exhibit low BOD to COD ratios (< 0.1) indicating non-biodegradable nature of dyes and Willmott et al. (1998) have claimed that aerobic biological degradation is not always effective for textile dye contaminated effluent (Sevimli & Sarikaya, 2002).

Somensia et al., (2010), tested pilot scale ozonation for the pre-treatment and colour removal of real textile effluent. Authors have mentioned that the importance of pH on the process efficiency and colour removal efficiencies were determined as 40.6% and 67.5% at pH 3.0 and 9.1, respectively. COD removal efficiencies were also determined as 18.7% (pH=3) and 25.5% (pH=9). On the other hand, toxicity can be reduced significantly compared with raw wastewater. Azbar et al., (2004) carried out a comparative study on colour and COD removal

from acetate and fiber dyeing effluent. In this study, various advanced oxidation processes (O_3 , O_3/UV , H_2O_2/UV , $O_3/H_2O_2/UV$, Fe^{+2}/H_2O_2) and chemical treatment methods using $Al_2(SO_4)_3 \cdot 18H_2O$, $FeCl_3$ and $FeSO_4$ for the Chemical Oxygen Demand (COD) and colour removal from a polyester and acetate fiber dyeing effluent is undertaken. Ozonation showed superior performance at pH=9 and 90% COD and 92% colour can be removed. Akal Solmaz et al., 2006, applied ozonation to real textile wastewaters and found 43% COD and 97% colour removal efficiencies at pH 9 and C_{O_3} 1.4 g/h. In the another study of Akal Solmaz et al., (2009), group has tested different AOPs on two different textile wastewater. 54-70% COD removal and 94-96 % colour removal efficiencies have been determined at pH = 9.

In another study, Selcuk, (2005), have tested coagulation and ozonation for color, COD and toxicity removal from textile wastewater. Author found that, ozonation was relatively effective in reducing colour absorbances and toxic effects of textile effluents compared with chemical coagulation. Almost complete colour absorbances (over 98%) were removed in 20 min ozone contact time, while COD removal (37%) was very low and almost stable in 30 min ozonation period.

Yonar et al., (2005), have been studied AOPs for the improvement of effluent quality of a textile industry wastewater treatment plant. Authors were mainly tested homogeneous photochemical oxidation processes (HPOP's) (H_2O_2/UV , O_3/UV and $H_2O_2/O_3/UV$) for colour and COD removal from an existing textile industry wastewater treatment plant effluent together with their operating costs. At pH=9, 81% COD and 97% colour removal efficiencies were reported for ozonation process.

As it can be clearly seen from literature, ozonation is very effective for the removal of colour from textile wastewater. COD and toxicity can also be removed by ozonation. But, for decision making on these processes advantages and limitations of these processes should be known. Main advantage of ozonation is no need to addition of any chemicals to water or wastewater. Because, ozone is mostly produced by cold corona discharge generators. And these generators need dry air for the production of ozone. On the other hand, sludge or similar residues is not produced during this process. At this point, specific advantage can be stated for textile effluents. Mostly, the pH value of textile wastewater are higher than 7 and in some situations higher than 9. Thus, ozonation can be applied to textile effluent without any pH adjustment and chemical addition. But, ozonation process has some disadvantages, such as, inefficient production capacities of cold corona discharge (CCD) generators (2-4%), less solubility of gas phase ozone in water, higher energy demands of CCD generators, possible emission problems of ozone etc. These disadvantages can be overcome by the production of efficient ozone generators like membrane electrochemical ozone generators.

Ozone/Hydrogen peroxide process is another efficient AOPs for the treatment of recalcitrant organics. Similar to ozonation, ozone including other processes mostly needs alkaline conditions. This argument has been extensively and successfully studied by Hoigne (1998) in the attempt of giving a chemical explanation to the short life time of ozone in alkaline solutions. Hoigne showed that the ozone decomposition in aqueous solution develops through the formation of hydroxyl radicals. In the reaction mechanism OH^- ion has the role of initiator:





It is clear therefore that the addition of hydrogen peroxide to the ozone aqueous solution will enhance the O_3 decomposition with formation of hydroxyl radicals. The influence of pH is also evident, since in the ozone decomposition mechanism the active species is the conjugate base HO_2^- whose concentration is strictly dependent upon pH. The increase of pH and the addition of H_2O_2 to the aqueous O_3 solution will thus result into higher rates of hydroxyl radicals production and the attainment of higher steady-state concentrations of hydroxyl radicals in the radical chain decomposition process (Glaze & Kang, 1989). It must be remarked that the adoption of the $\text{H}_2\text{O}_2/\text{O}_3$ process does not involve significant changes to the apparatus adopted when only O_3 is used, since it is only necessary to add an H_2O_2 dosing system (Andreozzi, 1998).

Hydrogen peroxide/ozone (peroxone) process test result for real or synthetic textile wastewater are too limited in literature but ozone and hydrogen peroxide is a very promising technique for potential industrial implementation. Kurbus et al. (2003) were conducted comparative study on different vinylsulphone reactive dyes. For all tested dyes, over 99% colour removal can be achieved at pH=12. Kos & Perkovski (2003), were tested different AOPs including peroxone process on real textile wastewater. Textile wastewater initial COD is over 5000 mg/L and authors declared that nearly 100% colour removal can be achieved with peroxone process. According to Akal Solmaz et al., (2006), addition of hydrogen peroxide to ozone is increased colour and COD removal efficiencies nearly 10%. Perkovski et al., (2003), were tested peroxone process on anthraquinone dye Acid Blue 62 and they found 60% colour removal efficiency.

Main advantage and disadvantage of peroxone process is addition of hydrogen peroxide. Addition of hydrogen peroxide is giving higher efficiencies and no need to upgrade the existing ozonation systems. But, addition of hydrogen peroxide means additional costs for the treatment of wastewater.

Finally, Fenton process is mostly applied on both textile and other industrial wastewaters. Nevertheless, the high electrical energy demand is general disadvantage of most AOPs. As it mentioned above, the greatest advantages of Fenton process is that no energy input is necessary to activate hydrogen peroxide. Most other AOPs need energy input for this activation such as UV based processes, US based processes, wet air oxidation etc.

The dark reaction of ferrous ion with hydrogen peroxide was found by Fenton (1894). During the last decades, important scientific studies were carried out on the treatment of most toxic chemicals and waste streams with this process. Another advantage of Fenton process is the applicability of this process in full scale. Because, this process can be accepted as the modification of traditional physico-chemical treatment. Fenton process can control in different steps of mixing and settling processes. By other words this process does not need

specific and complex reactor designs. But, the main important disadvantage of this process among all AOPs is sludge production. Ferric salts should be settled and disposed before discharge of the effluent.

Treatment efficiencies and results of applied Fenton process results in literature summarized in Table 1. According to these results, Fenton process is also promising technique for the treatment and decolorisation of textile effluent.

COD removal (%)	Colour removal (%)	pH	C _{H2O2} (mg/L)	C _{FeSo4} - C _{FeCl3} (mg/L)	Literature
64-71	78-95	3	200-400	200-400	Akal Solmaz et al. (2006)
43-58	92-97	3	100-200	150-200	Akal Solmaz et al. (2009)
84-87	90-91	3-3.5	200-250	200-250	Yonar (2010)
94	96	5	300	500	Azbar et al (2005)
59	89	3.5	800	300	Meriç et al (2005)
29	65	4	70	20	Üstün et al. (2007)
67	90	3-5	150	150	Lin et al. (1997)
93 (TOC)	99	2.45	5200	3600	Liu et al. (2007)
16-22	92-96	4	10	5	Kang et al. (2002)

Table 1. Results of Fenton process in literature in terms of COD and colour removal

4.2 Colour removal with photochemical AOPs

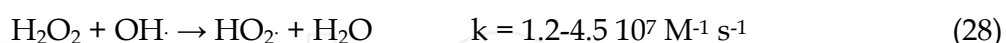
For the treatment and decolorisation of textile effluent, photochemical oxidation processes are widely investigated in literure. Photochemical oxidation processes are good and emerging alternatives and need UV radiation for the production of hydroxyl radicals. Vakuum UV phooxidation is most powerful member of these processes. Hydroxyl radicals can be produced with VUV with no any chemical addition. Generally Ve-eximer lamp are employed for VUV band radiation. In literature, a number of studies can be found for the treatment of organics with VUV. Despite numerous positive examples, the theory of reactor modelling for sharply nonuniform light distribution is not well developed (Braun et al., 1993). Main reason of this situation is the high price of Xe-eximer lambs.

Tarasov et al., (2003) investigated VUV photolysis for dye oxidation. They tested VUV process on 6 different dye solutions (methylene blue (Basic Blue 9), Basic blue Zn-salt; Direct Green 6; fucsine; Acid Yellow 42, Acid Yellow 11). Degradation of all dyes under VUV condition takes place in about a minute. In another study, Al-Momani et al. (2002) studied photo-degradation and biodegradability of three different families of non-biodegradable textile dyes (Intracron reactive dyes, Direct dyes and Nylanthrene acid dyes) and a textile wastewater, using VUV photolysis. Ninety percent of colour removal of dye solutions and wastewater is achieved within 7 min of irradiation.

UV/H₂O₂ is one of the popular and commercial advanced oxidation process. Like other AOPs, the reaction pH of the treatment system has been observed to significantly affect the degradation of pollutants (Sedlak & Andren, 1991, Lin & Lo, 1997, Kang & Hwang, 2000, Nesheiwat & Swanson, 2000, Benitez et al., 2001a). The optimum pH has been observed to be 3 in the majority of the cases in which H₂O₂ was used with UV irradiation (Ventakandri & Peters, 1993, Tank & Huang, 1996, Kwon et al., 1999, Benitez et al., 2001b) and hence is recommended as the operating pH. It should be noted here that the intrinsic rates of UV/H₂O₂ process may not be affected much, but at lower operating pH, the effect of the

radical scavengers, especially ionic such as carbonate and bicarbonate ions, will be nullified leading to higher overall rates of degradation. Thus, it is better to have lower operating pH (Gogate & Pandit, 2004b).

In literature, hydrogen peroxide (H_2O_2) itself acts as an effective hydroxyl radical ($\text{OH}\cdot$) scavenger at high concentrations given in following empirical equation (Arslan, 2000).



Although $\text{HO}_2\cdot$ promoted radical chain reactions and it is an oxidant itself, its oxidation potential is much lower than that of hydroxyl radical ($\text{OH}\cdot$). Thus, the presence of excess hydrogen peroxide (H_2O_2) can lower the treatment efficiency of AOPs and it is very important to optimize the applied hydrogen peroxide (H_2O_2) concentration to maximize the treatment performance of AOPs (Arslan, 2000).

The presence in the treated water of carbonate can result in a significant reduction of the efficiency of abatement of pollutants as explained in some studies (Bhattacharjee & Shah, 1998, Andreozzi et al., 1999). Carbonate acts as radical scavenger;



since $\text{CO}_3^{\cdot-}$ is much less reactive than hydroxyl radical ($\text{OH}\cdot$) inhibition by carbonate influences the behavior of most AOPs. At lower operating pH values, the effect of radical scavengers, especially ionic such as carbonate and bicarbonate will be nullified leading to higher overall rates of degradation (Gogate & Pandit, 2004a). Thus, lower operating pH values are recommended for most AOPs in literature. Galindo & Kalt, (1998) documented that the $\text{H}_2\text{O}_2/\text{UV}$ process was more effective in an acid medium ($\text{pH} \approx 3\text{--}4$) in term of discoloration.

On the other hand, the aqueous stream being treated must provide good transmission of UV light, so that turbidity and high suspended solids concentration would not cause interferences. Scavengers and excessive dosages of chemical additives may inhibit the process. Heavy metal ions (higher than 10 mg l^{-1}), insoluble oil and grease, high alkalinity and carbonates may cause fouling of the UV quartz sleeves. Therefore, a good pretreatment of the aqueous stream should be necessary for UV based AOPs (Azbar et al, 2005).

Decolorisation and treatment of textile effluent were investigated in most studies (Shu et al., 1994, Galindo & Kalt, 1998, , Arslan and Balcioglu, 1999, Ince, 1999, Neamtu et al., 2002, Cisneros, 2002, Mohey El-Dein et al., 2003, Azbar et al, 2004, Shu & Chang, 2005, Yonar et al. 2005). According to these studies, the use of $\text{H}_2\text{O}_2/\text{UV}$ process seems to show a satisfactory COD (70-95%) and colour(80-95%) removal performance.

According to Rein (2001), conventional ozonation of organic compounds does not completely oxidize organics to CO_2 and H_2O in many cases. Remaining intermediate products in some solution after oxidation may be as toxic as or even more toxic than initial compound and UV radiation could complete the oxidation reaction by supplement the reaction with it. UV lamp must have a maximum radiation output 254 nm for an efficient ozone photolysis. The O_3/UV process is more effective when the compounds of interest can be degraded through the absorption of the UV irradiation as well as through the reaction with hydroxyl radicals (Rein, 2001; Metcalf and Eddy, 2003). The O_3/UV process makes use of UV photons to activate ozone molecules, thereby facilitating the formation of hydroxyl radicals (Al-Kdasi et al., 2004).

Hung-Yee & Ching-Rong (1995) documented O_3 /UV as the most effective method for decolorizing of dyes comparing with UV oxidation by UV or ozonation alone. While, Perkowski & Kos (2003) reported no significant difference between ozonation and O_3 /UV in terms of colour removal. Even though ozone can be photodecomposed into hydroxyl radicals to improve the degradation of organics, UV light is highly absorbed by dyes and very limited amount of free radical ($HO\cdot$) can be produced to decompose dyes. Thus same colour removal efficiencies using O_3 and O_3 /UV could be expected. In normal cases, ozone itself will absorb UV light, competing with organic compounds for UV energy. However, O_3 /UV treatment is recorded to be more effective compared to ozone alone, in terms of COD removal. Bes-Piá et al. (2003) documented that O_3 /UV treatment of biologically treated textile wastewater reduced COD from 200-400 mg/L to 50 mg/L in 30 minutes, while, using ozone alone COD reduced to 286 mg/L in same duration. Azbar et al. (2004) documented that using O_3 /UV process high COD removal would be achieved under basic conditions (pH=9). Yonar et al. also reported that using O_3 /UV process showed high COD removal efficiency under similar conditions (pH=9) for physically and biologically treated textile effluent.

The addition of H_2O_2 to the O_3 /UV process accelerates the decomposition of ozone, which results in an increased rate of $OH\cdot$ generation (Teccommentary, 1996). In literature most AOPs applied for the treatment of textile effluent and, among the all applied AOPs for dye house wastewater, acetate, polyester fiber dyeing process effluent and treatment plant outlet of textile industry with the combination of H_2O_2 / O_3 /UV appeared to be the most efficient in terms of decolouration (Perkowski & Kos, 2003, Azbar et al., 2004, Yonar et al, 2006).

The rate of destruction of organic pollutants and the extent of mineralisation can be considerably increased by using an $Fe(II,III)/H_2O_2$ reagent irradiated with near-UV and/or visible light (Goi & Trapio, 2002, Torrades et al., 2003, Liou et al., 2004, Murugunandham & Swaminathan, 2004), in a reaction that is called the "photo-Fenton reaction". This process involves the hydroxyl radical ($HO\cdot$) formation in the reaction mixture through photolysis of hydrogen peroxide (H_2O_2 /UV) and fenton reaction (H_2O_2/Fe^{+2}) (Fenton, 1894; Baxendale and Wilson, 1956). Using the photo-fenton process to treat dye manufacturing wastewater, which contains high strength of color, and the results demonstrated its great capability for colour removal (Kang et al., 2000; Liao et al., 1999). Since the hydroxyl radical is the major oxidant of the photofenton process, the removal behavior of COD and colour is highly related with the hydroxyl radical formation. However, the relation between the removal of COD and colour with the hydroxyl radical formation in the decolorisation of textile wastewater by photo-fenton process was rarely found in the literature.

The colour removal is markedly related with the amount of hydroxyl radical formed. The optimum pH for both the hydroxyl radical formation and colour removal occurs at pH 3 ± 5 . Up to 96% of colour can be removed within 30 min under the studied conditions. Due to the photoreduction of ferric ion into ferrous ion, colour resurgence was observed after 30 min. The ferrous dosage and UV power affect the colour removal in a positive way, however, the marginal benefit is less significant in the higher range of both (Kang et al., 2000)

Liu et al., 2007 investigated the degradation and decolorisation of direct dye (Everdirect supra turquoise blue FBL), acidic dye (Isolan orange S-RL) and vat dye (Indanthrene red FBB) by Fenton and UV/Fenton processes. A comparative study for Fenton and UV/Fenton reactions by photoreactor has been carried out by scale-up of the optimum conditions, obtained through jar-test experiments. Fenton process is highly efficient for colour removal for three dyes tested and for TOC removal of FBB and FBL. The optimum pH values

obtained were all around 3 for FBL, FBB and S-RL. UV/Fenton process improved slightly for FBB and FBL treatment efficiencies compared to Fenton reaction while S-RL showed much better improvement in TOC removal.

The photolysis and photo-catalysis of ferrioxalate in the presence of hydrogen peroxide with UV irradiation (UV/ferrioxalate/H₂O₂ process) for treating the commercial azo dye, reactive Black B (RBB), is examined. An effort is made to decolorize textile effluents at near neutral pH for suitable discharge of waste water. pH value, light source, type of initial catalyst (Fe³⁺ or Fe²⁺) and concentration of oxalic acid (Ox) strongly affected the RBB removal efficiency. The degradation rate of RBB increased as pH or the wavelength of light declined. The optimal molar ratio of oxalic acid to Fe(III) is three, and complete colour removal is achieved at pH 5 in 2 h of the reaction. Applying oxalate in such a photo process increases both the RBB removal efficiency and the COD removal from 68% and 21% to 99.8% and 71%, respectively (Huang et al., 2007)

Neamtu et al. (2004) investigated the degradation of the Disperse Red 354 azo dye in water in laboratory-scale experiments, using four advanced oxidation processes (AOPs): ozonation, Fenton, UV/H₂O₂, and photo-Fenton. The photodegradation experiments were carried out in a stirred batch photoreactor equipped with an immersed low-pressure mercury lamp as UV source. Besides the conventional parameters, an acute toxicity test with a LUMISTox 300 instrument was conducted and the results were expressed as the percentage inhibition of the luminescence of the bacteria *Vibrio fischeri*. The results obtained showed that the decolorisation rate was quite different for each oxidation process. After 30 min reaction time the relative order established was: UV/H₂O₂/Fe(II) > Dark/H₂O₂/Fe(II) > UV/H₂O₂/O₃ > UV/H₂O₂/Lyocol. During the same reaction period the relative order for COD removal rate was slightly different: UV/H₂O₂/Fe(II) > Dark/H₂O₂/Fe(II) > UV/H₂O₂ > UV/H₂O₂/Lyocol > O₃. A colour removal of 85% and COD of more than 90% were already achieved after 10 min of reaction time for the photo-Fenton process. Therefore, the photo-Fenton process seems to be more appropriate as the pre-treatment method for decolorisation and detoxification of effluents from textile dyeing and finishing processes. Sulphate, nitrate, chloride, formate and oxalate were identified as main oxidation products.

Liu et al., (2010), evaluated the photocatalytic degradation of Reactive Brilliant Blue KN-R under UV irradiation in aqueous suspension of titanium dioxide under a variety of conditions. The degradation was studied by monitoring the change in dye concentration using UV spectroscopic technique. The decolorisation of the organic molecule followed a pseudo-first-order kinetics according to the Langmuir-Hinshelwood model. Under the optimum operation conditions, approximately 97.7% colour removal was achieved with significant reduction in TOC (57.6%) and COD (72.2%) within 3 hours. In another study, Bergamini et al., (2009), investigated photocatalytic (TiO₂/UV) degradation of a simulated reactive dye bath (Black 5, Red 239, Yellow17, and auxiliary chemicals). After 30 min of irradiation, it was achieved 97% and 40% of colour removal with photocatalysis and photolysis, respectively. No mineralisation occurred within 30 min.

According to photocatalytic decolorisation studies, high rate of organic and color removal can be achieved. The main advantage of these processes is the usage of solar light. In another words, there is no energy need for hydroxyl radical production. But, removal and recycling of semiconductors (TiO₂, ZnO etc.) from aqueous media is very important for both cost minimisation and effluent quality.

Finally, for true and good decision making on the treatment process, cost of all the compared processes should be calculated. In next step, cost evaluation of these processes are evaluated.

4.3 Cost evaluation of AOPs for colour removal

Cost evaluation is an important issue for decision making on a treatment process as much as process efficiency. Actual project costs can not be generalized; rather they are site-specific and thus must be developed for individual circumstances (Qasim et al., 1992). For a full-scale system, these costs strongly depend on the flow rate of the effluent and the configuration of the reactor as well as the nature of the effluent (Azbar et al., 2004). From these reasons, complete cost analysis of an AOP including treatment plant flow chart is too limited in literature. Azbar et al. 2005, Solmaz et al, Ustun et al, Yonar et al and Yonar, 2010 tried to explain the operational costs of examined AOPs. Average costs of applied processes are given in Table 2.

Process Type	Operational Cost (USD/m³)
Coagulation	0,07-0,20
Ozonation	4,21-5,35
Fenton process	0,23-0,59
Fenton-like process	0,48-0,57
Peroxane	5,02-5,85
UV/H ₂ O ₂	1,26-4,56
UV/O ₃	6,38-8,68
UV/O ₃ /H ₂ O ₂	6,54-11,25

Azbar et al. 2005, Solmaz et al, Ustun et al, Yonar et al 2005 and Yonar, 2010

Table 2. Average operational costs of AOPs

In another study of Yonar 2010, treatment plant cost calculations were carried out according to Turkey conditions. The overall costs are represented by the sum of the capital costs, the operating costs and maintenance. For a full-scale system (200 m³/day, hand-printed textile wastewater), these costs strongly depend on the flow-rate of the effluent and the configuration of the reactor as well as the nature of the effluent (Azbar et al., 2004). Conventional treatment system (physical/ chemical/ biological treatment processes) and Fenton process (physical/Fenton processes) costs are summarized in this section for a meaningful explanation.

4.3.1 Capital costs

Capital costs of a treatment plant were calculated in four sub-stages: (1) constructional, (2) mechanical, (3) electrical, and (4) other costs.

Constructional costs of both treatment flow charts were computed by a Civil Engineering Office according to environmental design results. Constructional costs include excavation, reinforced concrete, buildings, excavator and crane rentals, electricity and labour costs. Land costs were excluded from the computations for the reason of industry own site usage. Mechanical and electrical costs are another chief and important capital costs for a treatment plant. Mechanical costs were determined by summing the costs of mechanical equipment purchase (coarse and fine screens, pumps, dosage pumps, mixers, chemical storage and handling tanks, blowers, diffusers, tank skimmers, filter-press etc.), pipes and fittings, material transportation and mechanical labour. Electrical costs contain automation, wiring, sensors (flow, pH, oxygen, ORP, level switches etc.) and electrical labour. Finally, other costs incorporate engineering design fee, charges and taxes, and profit and overhead. All

equipment and material prices and labour costs were collected from different treatment plant equipment suppliers and engineering offices in Turkey.

ITEM	CAPITAL COSTS (Euro)	
	Conventional Treatment System	Fenton Process Treatment System
Construction Costs		
• Basin Constructions ¹	27 500 €	19 000 €
• Building Constructions ^{1,2}	13 000 €	13 000 €
• Rentals	6 300 €	4 700 €
• Electricity ³	850 €	700 €
Mechanical Costs		
• Physical Unit Equipments ⁴	10 800 €	10 800 €
• Chemical Unit Equipments ⁴	12 800 €	23 500 €
• Biological Unit Equipments ⁴	12 600 €	-
• Disinfection Unit Equipments ⁴	700 €	-
• Sludge Unit Equipments ⁴	15 500 €	15 500 €
• Piping Costs ⁴	9 500 €	4 000 €
• Transportation and Rentals	2 500 €	2 000 €
Electrical Costs		
• Automation ⁵	7 500 €	7 000 €
• Wiring ⁵	1 500 €	1 500 €
• Sensors and Switches	3 600 €	2 200 €
SUB-TOTAL - A	124 650 €	103 900 €
Other Costs		
• Engineering Fee (5% of sub-total a)	6 233 €	5 195 €
• Charges	2 000 €	2 000 €
• Profit and overhead (15% sub-total a)	18 698 €	15 585 €
SUB-TOTAL - B	151 581 €	126 680 €
Taxes (VAT: 18% of sub-total - b)	27 285 €	22 803 €
TOTAL	178 866 €	149 483 €

¹All construction costs include labour costs
²Buildings are designed (pre-fabric 200 m² closed area) as same capacity for both treatment plants including a small laboratory, chemical preparation and dosage units, blowers (for biological treatment unit) and sludge conditioning and filter-press units.
³1 kW = 0.087 Euro
⁴All mechanical costs include labour costs
⁵All electrical costs include labour costs

Table 3. Capital Cost Estimates of Conventional (Physical/Chemical/Biological) and Fenton Process (Physical/Fenton Process) Treatment Plants

Table 3 presents capital cost estimates for the conventional and Fenton process treatment plants designed on the basis of 200 m³/day. As shown in this table, the total capital cost estimates for conventional treatment plant and Fenton process treatment plant are 178 866 and 149 483 Euro, respectively. All equipment costs were provided including 2 years non-prorated warranty by all suppliers. But, sensors, switches and other spare parts were excluded from warranty. It can clearly be observed from the cost analysis that the specific costs for Fenton process treatment plant are about 16% lower than that of the conventional treatment plant alternative. On the other hand, constructional costs of the conventional treatment system are higher than Fenton process treatment alternative. But, mechanical and electrical capital cost trends can be regarded identical for both treatment alternatives. These cost differences originate from biological treatment unit, because activated sludge tank entails great construction area and more mechanical work effort.

4.3.2 Operation and maintenance costs

Operation and maintenance costs (O&M) include power requirement, chemicals, spare parts, wastewater discharge fees, plant maintenance and labour. Textile industry wastewater treatment plant sludges are accepted as a toxic and hazardous waste in Turkish Hazardous Wastes Control Regulations (Anonymous, 2005). Therefore, toxic and hazardous waste disposal costs and charges strongly depend on disposal technology and locations of the treatment plant and hazardous waste disposal plants. For these reasons, only sludge disposal costs were excluded from O&M cost estimations.

ITEM	Operating and Maintenance Costs (Euro/m ³)	
	Conventional Treatment System	Fenton Process Treatment System
• Electrical power for processes and other facilities	0.24	0.17
• Spare part costs	0.04	0.03
• Chemicals	0.70	0.81
• Labour	0.34	0.34
• SUB-TOTAL	1.32	1.35
• Equipment repair, replacement and overhead (10% of sub-total)	0.13	0.135
TOTAL	1.452	1.485
REAGENT PRICES	<i>Unit</i>	<i>Price (Euro)</i>
• Hydrogen peroxide	Kg	0.55
• Sulphuric Acid	Kg	0.85
• Sodium Hydroxide	Kg	0.75
• Ferric Chloride	Kg	1.95
• Ferrous Sulphate	Kg	1.05
• Sodium Hypochlorite	Kg	0.20
• Polymer	Kg	2.35
• Electricity	kWh	0.087

Table 4. O&M costs of the studied treatment methods (cost of sludge disposal was excluded)

On the other hand, labour costs are very important part of O&M costs. Labour costs are facility-specific, and depend on the size, location and plant design. Therefore, labour costs may vary substantially (Pianta et al., 2000). These treatment plants can be considered as small treatment plants because of 200 m³/day flow capacity. Accordingly, 9 working hours per day and a salary of 18 Euro/day (equal to minimum wage) for 2 workers and 32 Euro/day for operator and/or engineer were presumed, and the labour costs were calculated using a fixed rate of 0,34 Euro/m³. Similar to labour costs, electricity and chemical prices are also country-specific. As shown in Table 3, the total costs of both conventional and Fenton process treatment plants were estimated as 1.452 Euro/m³ and 1.485 Euro/m³. According to these results, Fenton process treatment system O&M costs are slightly (3%) higher than conventional treatment system owing to relatively higher chemical usage of Fenton process treatment system. However, capital cost difference of both systems may afford operating cost difference for 15 years. The labour costs constitute about 23% of the overall O&M costs. On the other hand, electricity appears to be another important cost value for conventional system. Consequently, Fenton process has shown superior treatment and colour removal performances, and can be accepted as more economical choice for hand-printed textile wastewater treatment.

5. Conclusions

Advanced Oxidation Processes are promising alternative of traditional treatment processes for the treatment of textile effluent. Removal of colour and recalcitrant organic content of textile effluent can be achieved with the high efficiencies. Costs of AOPs are another point of view. In most cases, capital and operation and maintenance cost of AOPs are generally higher than traditional processes. But, Fenton process seems to be viable choice for textile wastewater treatment.

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